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Investigations on copolymer formation through ultrasonic and viscosity measurements

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Abstract : Ultrasonic and viscosity measurements have been employed to study the copolymer formation between proton donor and proton acceptor molecules of Polyvinyl Chloride (PVC) and Polystyrene (PS) molecules respectively Tetrahydrofuran (THF) has been used as a common solvent Measurements have been made at three different temperatures 30°, 35° and 40°C Maxima or minima in the properties studied have been used to predict copolymer formation.

Keywords : Ultrasonic velocity, viscosity, PVC-PS, donor-acceptor, copolymers

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1. Introduction

Extensive use of polymeric materials in technology has led in recent years to the increased interest to the various problems of the Physics and Chemistry of polymers. Few attempts seem to have been made to use acoustics as a tool in studying physical properties of polymers. Degradation of polymers subjected to ultrasonic waves has been reported to occur by Gowarikar *et al* [1]. Velocity of ultrasonic waves has been measured by Swarup and Chandra [2] in xylene solutions of phenolic and silicon resins, and a few physical parameters have been calculated. Malikarjuna Reddy *et al* [3] have measured thermo-acoustic properties of polymers at low temperature using theoretical model proposed by Sharma and Reddy [4–7]. Donor-acceptor interaction in binary system of trichloromethane with ethylacetate has been interpreted to lead to the formation of 1 : 1 intermolecular complex by Oswal [8], using dielectric and refractive index measurements. The functional groups participate in the formation of coordinate covalent bond, namely the proton donor and proton acceptor groups. Polyvinyl chloride (PVC) belongs to compounds of proton donor groups called class-A [9], while polystyrene (PS) belongs to a proton acceptor group called class-B [9]. As such, in order to study the interaction between donor-acceptor molecules, samples of PVC and PS have been used with tetrahydrofuran as an inert solvent.

2. Sample preparation

Two polymeric solids namely PVC and PS were dissolved in THF so that weight fraction of total solute in THF is of the order of 0.015. The relative concentration of the two solutes were changed in definite proportions. Eight samples were prepared and measurements were taken at three different temperatures.

3. Experimental details

Ultrasonic interferometer has been employed to measure ultrasonic velocity in sample solutions at fixed frequency 2 MHz. Viscosity measurements have been made by using an Ostwald viscometer. Temperatures have been kept constant using constant temperature water bath. Density measurements have been made using a density bottle and monopan balance. Accuracy in the measurements of ultrasonic velocity is ± 0.5%. Temperature can be kept constant to an accuracy of 0.1°C. Accuracy in the measurement of viscosity and density have been ascertained by measuring viscosity and density of known liquids and comparing them with literature values. Values of ultrasonic velocity, density and viscosity of the samples have been measured at three different temperatures, 30°C, 35°C and 40°C. Values of adiabatic compressibility β, specific acoustic impedence Z and viscosity η have been calculated using relations.

$$\beta_a = 1/U^2\rho \tag{1}$$

$$Z_{expt} = U_{expt}\,\rho_{expt} \tag{2}$$

$$\eta = \left(\rho_s t_s / \rho_w t_w\right)\eta_w \tag{3}$$

where U = Ultrasonic velocity, η_w = viscosity of water, ρ_s and ρ_w = densities of solutions and water respectively and t_s and t_w = time of fall between specific marks on viscometer for solution and water respectively.

Values of β_a, Z and η at different temperatures have been entered in Tables 1, 2 and 3.

Table 1. Values of U, β_a, Z and η at different weight fractions of PVC/PS at 30°C.

S N	Velocity (cm/s)	$\beta_a \times 10^{12}$ cm²/dyne	Z_{expt} dyne-S/cm³	$\eta \times 10^2$ Poise	Wt fraction of PVC	Wt. fraction of PS
1	125050	72.22	110720	1 0448	0.0149	0.0000
2	124680	72.57	110512	1 2282	0.0131	0.0020
3	124440	72.87	110274	1.1049	0.0113	0.0037
4	124000	73.39	109872	1.1028	0.0094	0.0057
5	125840	71 33	111404	1.0758	0.0074	0.0076
6	125552	71 66	111137	1.1115	0.0055	0.0093
7	125120	72.19	110706	0.9439	0.0037	0.0113
8.	125680	71.87	110706	0.8749	0.0000	0.0150

Table 2. Values of U, β_a, Z and η at different weight fractions of PVC/PS at 35°C

S N	Velocity (cm/s)	$\beta_a \times 10^{12}$ cm²/dyne	Z_{expt} dyne-S/cm³	$\eta \times 10^2$ Poise	Wt fraction of PVC	Wt. fraction of PS
1.	124120	75 95	108940	1 1005	0 0150	0.0000
2.	123580	74 73	108278	0 6284	0 0131	0 0018
3	123600	74 56	107975	1 0741	0 0114	0 0037
4	123520	74.71	108359	1 9974	0 0094	0.0057
5	123680	74.50	108524	1 0718	0 0075	0.0075
6.	124000	74 12	108708	1 8595	0 0056	0 0093
7	123280	75 28	107750	0 9383	0 0037	0 0113
8.	123640	74 84	108065	0 9371	0 0000	0 0150

Table 3. Values of U, β_a, Z and η at different weight fractions of PVC/PS at 40°C.

S N.	Velocity (cm/s)	$\beta_a \times 10^{12}$ cm²/dyne	Z_{expt} dyne-S/cm³	$\eta \times 10^2$ Poise	Wt fraction of PVC	Wt fraction of PS
1	121520	77 18	106615	0 7240	0.01514	0 0000
2.	121280	77 34	106688	0 8793	0 01325	0 0017
3	120640	78 17	106034	0 8882	0 0113	0 0037
4	120600	80 88	103972	0 8541	0 0094	0 0057
5.	121900	76 50	107099	0 9255	0 0075	0 0076
6.	120600	78 16	105666	0.7621	0 0056	0 0094
7.	188800	81 19	103595	0 6906	0 00000	0 0151

4. Results and discussion

It can be seen from the Tables 1-3 that ultrasonic velocity U, specific acoustic impedence Z and viscosity η of the sample mixtures show a maximum, at or very near the equi-weight fractions of the constituent and the adiabatic compressibility β_a shows a minimum there. Further, the maximum velocity U_{max}, maximum specific acoustic impedence Z_{max} and maximum viscosity η_{max} decrease with increase of temperature; β_a shows an opposite type of behaviour.

These experimental observations can be explained on the basis of complex formation through coordinate covalent-bonding between the constituents of the mixture.

The presence of the electro-negative chlorine atom in PVC is responsible for activating the hydrogen atom in the molecule. Chlorine being highly electronegative, attracts the shared electron towards itself creating a partial charge δ^+ on C-atom. The charge δ^+ on C-atom will

attract the electron pair shared between the two C-atoms, thereby developing a charge δ^+ on second carbon atom as shown in Figure 1.

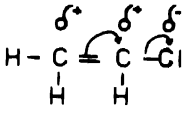

Figure 1.

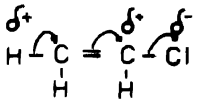

Figure 2.

The second carbon atom being attached to two hydrogen atoms, it will pull the shared electron pair to itself. This makes the H-atom to develope an effective charge δ^+ which is the proton available as a donor proton. This is shown in Figure 2.

Polystyrene contains a proton acceptor group (such as ketones, aldehyde, ethers, esters, tertiary amines, olefines, benzene and other aromatic compounds). The presence of the aromatic ring imparts this characteristic. By accepting the incoming proton, the styrene gets more stabilised by forming a carbonium ion which is more stable than styrene due to the delocalisation of the +ve charge over the benzene ring by resonance mechanism.

Thus, with the availability of the proton group in PVC and proton acceptor group in PS, there is every likelihood of the formation of coordinate covalent bond between PVC and PS, giving rise to the copolymer formation.

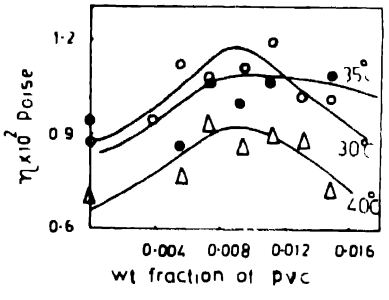

Figure 3. Variation of viscosity η of sample solutions with weight fractions of PVC at different constant temp

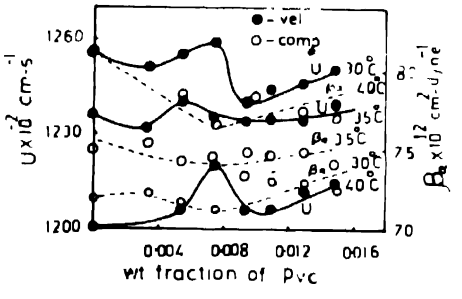

Figure 4. Variation of ultrasonic velocity U and adiabatic compressibility β_a of sample solutions with weight fractions of PVC at different constant temperatures.

It is such copolymer species which will be statistically expected to be formed in large numbers at or very near the equal concentrations of the donor-acceptor species. These copolymeric formations might be responsible for sudden change in the behaviour of the sample mixtures at or very near the equal concentration.

Strepikheyers *et al* [10] have reported the formation of graft copolymers in polyvinyl acetate with polyethylene in the sidechain, polymethyl acrylate with poly-n-chlorostyrene in the sidechain, polystyrene with polyvinyl chloride in the sidechain.

The bulkier copolymer molecules will naturally exhibit greater viscosity and geater specific acoustic impedence than the individual molecules, giving rise to maximum in η and z.

Similarly, the adiabatic compressibility will decrease with bulkier molecules resulting in a minimum in β_a.

Increase in energy of vibration accompanied with rise of temperature should be reflected in a decrement in the maximum values of η, z and U and increment in the maximum value of compressibility β_a of the sample mixtures.

5. Conclusion

It therefore follows that the experimental findings can thus be satisfactorily explained on the basis of copolymer formation through coordinate covalent bonding between donor and acceptor molecules employing ultrasonic and viscosity measurements.

Further work in isolating the copolymeric species and studying its characteristic physical and chemical properties is of interest and is being shortly undertaken in this laboratory.

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